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PATENT SPECIFICATION

(11) 1 449 091

(21) Application No. 18954/74 (22) Filed 30 April 1974
(31) Convention Application No. 23558
(32) Filed 30 April 1973 in
(33) Italy (IT)
(44) Complete Specification published 8 Sept. 1976
(51) INT CL² C07D 301/08
(52) Index at acceptance
C2C 1301 215 246 247 253 25Y 304 305 30Y 411 413 414 416 458 ZA

(19)

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(54) PROCESS FOR PARTIALLY OXIDISING ORGANIC COMPOUNDS

(71) We, SNAMPROGETTI, S.P.A., formerly Snam Progetti S.p.A., an Italian Company, of Corso Venezia, 16, Milan, Italy, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a process for carrying out partial oxidation with oxygen of ethylenically unsaturated compounds (for example ethylene), in the vapour phase.

More particularly, but not exclusively, the present invention relates to a process for the partial oxidation in the vapour phase with O_2 of ethylene to ethylene oxide. Hereinafter, in the description, reference will be made, for the sake of simplicity, to the partial oxidation with O_2 of ethylene to ethylene oxide, although it will be appreciated that the process is suitable for carrying out the partial oxidation of other ethylenically unsaturated compounds.

It is known that a process for the production of ethylene oxide from ethylene and oxygen can be carried out in a plant as shown in Figure 1 of the accompanying drawings. In this plant, the reaction occurs in a reactor 61 provided with a bundle of tubes within a shell; the catalyst is placed inside the tubes; to remove the heat of reaction, a heat exchange fluid circulates within the reactor shell; this fluid is cooled in a heat exchanger 62 in which steam is produced. A pump 63 is used to circulate the fluid; this arrangement is used if the heat exchange fluid is maintained in the liquid state; in the case that used is made of an evaporating fluid, the pump 63 can be eliminated since it is possible to rely on a gravity circulation. An example of an evaporating fluid is water; in such a case the heat exchanger 62 can also be eliminated, and steam produced directly in the shell of the reactor 61.

The gaseous reaction product leaving the reactor 61 is used to heat the gas fed to the same reactor 61, by means of a heat exchanger 64, and then the gaseous reaction product is fed to a column 65 wherein ethylene oxide is absorbed by a suitable solvent, for example water, introduced through an inlet 70. The gaseous reaction product, after absorption of the oxide, is recycled to the reactor 61 by means of a compressor 66. Introduced into gas being recycled to the reactor 61 are fresh reagents; in fact ethylene and the oxidizing agent (air or oxygen), are introduced through inlets 67 and 68, respectively.

To avoid the accumulation in the plant of the inert gases which enter at the same time as the reagents, a small quantity of gas is vented through a pipe 69. In the case of plants fed with air, the ethylene contained in the exhaust gases can be fed to a subsidiary system analogous to that described above; in the case of plants fed with oxygen, in the cycle, a means for absorbing carbon dioxide can be included; carbon dioxide is an undesired by-product of the partial oxidation of organic compounds. Both heat exchangers 62 and 64 constitute essential components in the plant for carrying out the known process. The production of steam in the heat exchanger 62 is a not inconsiderable feature of the plant economy, since it can be used in the plant itself for producing energy or can be used outside the plant. Also the heat exchanger 64 has an essential function, namely the recovery of heat from the effluent stream for heating the influent stream being fed to the reactor 61.

It is to be noted, however, that the heat exchanger 64 is in such a position that the reagents fed to the reactor 61 are at high temperature for all the time that they are in the pipe between the heat exchanger 64 and the reactor inlet. A consequence of this is that the O_2 content of the feed mixture must be less than that corresponding to the flammability limit at the temperature obtaining, that is at most 7—8% by volume.

In the known process the reaction mixture is fed to the reactor 61 at the highest possible temperature, after having been preheated in the heat exchanger 64, by the reaction mixture leaving the reactor 64. As the reaction is exothermic, it is possible to produce a large amount of steam by exploiting the heat of reaction. As indicated above, it is only possible to use low oxygen concentrations in the reaction mixture entering the reactor 61 because of the risk of explosion; consequently the concentration of the desired oxidized compound in the mixture leaving the reactor 61 is low and therefore large reactors are necessary, large volumes of gaseous mixtures must be circulated and compressed and furthermore the system for recovering the oxidized compound is expensive.

According to one aspect of the present invention, there is provided a process for producing an epoxide by partially oxidizing an ethylenically unsaturated compound in the vapour phase with oxygen or a gaseous mixture including oxygen, which process comprises (a) passing a mixture of (i) the ethylenically unsaturated compound and (ii) oxygen or a gaseous mixture including oxygen through a heating zone containing bodies of inert materials, so as to cause, by means of heat exchange, the temperature of the mixture of (i) and (ii) to be in the range from 100°C to 300°C; (b) passing the heated mixture through a reaction zone which contains an oxidation catalyst and in which the partial oxidation of the ethylenically unsaturated compound is carried out, the reaction zone being contiguous to the heating zone without any break in continuity; and (c) passing the resulting reaction products from the reaction zone through a cooling zone in which the products are cooled by means of heat exchange to a temperature lower than 150°C, the cooling zone being contiguous or not contiguous to the reaction zone and containing or not containing bodies of inert material, and the heat withdrawn in the cooling zone being utilized in the heating zone.

It has been found that the concentration of oxygen in the influent mixture at the inlet of the reaction zone can be increased and consequently all the aforementioned drawbacks reduced, by carrying out the preheating of the reaction mixture of ethylene (or other ethylenically unsaturated compound) and oxygen at high concentration through heat exchange with a hot fluid in a heating zone adjacent to, and upstream of, the reaction zone. The heating zone is preferably constituted by a bundle of tubes, and it is in any case provided with a filling which is inert with respect to the reagents. The oxygen can be present in the reaction mixture in a concentration up to 20% by volume. This reaction mixture is heated in the heating zone by means of heat exchange from, say, ambient temperature to the desired temperature, generally in the range from 100 to 300°C, especially in the range from 180 to 220°C.

The reaction zone is preferably constituted by a bundle of tubes, and is in any case filled with a catalyst, whereas the cooling zone, which is preferably constituted by a bundle of tubes, may or may not have a filling of inert material. When the cooling zone is not contiguous to the reaction zone, i.e. the two zones are separated from each other, the inert filling is preferably absent.

The different zones can be portions of the same bundle of tubes.

The bodies of inert materials can be, for example, small cylinders, small spheres, or Raschig rings; preferably the voids present in the heating and cooling zones constitute less than 50% by volume of the volume of the respective zone.

When the cooling and heating zones are constituted by a bundle of tubes, the ratio between the maximum dimension of one of the filling bodies and the internal diameter of the tubes is preferably not greater than 0.40:1; more preferably the ratio is in the range from 0.30:1 to 0.36:1.

This process of the present invention can be carried out in an apparatus which comprises a reactor having a shell in which is located a bundle of tubes, divided by two or more baffles into three or more zones, the bundle of tubes having its ends terminating in plates to which the shell end caps are joined, there being a cooling circuit for an intermediate zone and one or more circuits for heating a zone at one end region of the reactor at the expense of heat withdrawn during cooling a zone at the other end region of the reactor, those regions of the tubes in the intermediate zone being filled with catalyst, those regions of the tubes in the heating zone(s) being filled with inert material and those regions of the tubes in the cooling zone(s) being filled or not filled with inert material.

One embodiment of the aforementioned apparatus is that wherein the reactor is divided by two baffles into three zones, and wherein a circuit is provided for conveying a heat transfer fluid from the uppermost zone to the lowermost zone and back to the uppermost zone.

An alternative embodiment of the aforementioned apparatus is that wherein the reactor is divided by 2N baffles into 2N+1 zones, where N is an integer greater than 1, and wherein one circuit links the uppermost and lowermost zones, and another circuit links the zone adjacent the lowermost zone with the zone adjacent the uppermost zone, and, where N exceeds 2, one or more additional circuits each link corresponding heating and cooling zones.

Alternatively the process of the present in-

vention can be carried out in a different apparatus which comprises a reactor having a shell in which is located a bundle of tubes, divided by a baffle into two zones, the bundle of tubes having its ends terminating in plates to which the shell end caps are joined, there being a cooling circuit for the upper zone and a circuit for heating the lower zone at the expense of heat withdrawn during cooling of reaction products at a point downstream of the reactor, those regions of the tubes in the upper zone being filled with catalyst and those regions of the tubes in the lower zone being filled with inert material.

The various apparatuses which are described above and which are suitable for carrying out the process of the present invention are claimed in our copending Patent Application No. 5222/76 (Serial No. 1,449,092).

For a better understanding of the present invention and to show how the same can be carried into effect, reference will now be made, by way of example, to Figures 2 to 6 of the accompanying drawings, in which:—

Figure 2 is a side view, on an enlarged scale, of a tube of a reactor in the plant of Figure 3;

Figure 3 represents a plant for carrying out the process of the present invention;

Figure 4 is a side view, on an enlarged scale, of a tube of a reactor in the plant of Figure 5;

Figure 5 represents another plant for carrying out the process of the present invention; and

Figure 6 represents a different plant for carrying out the process of the present invention.

In Figure 2 there is shown a single tube of the reactor 1 of the plant of Figure 3; the heating of the reagents is effected in a lower portion 12, the reaction occurs in an intermediate portion 4 and in an upper portion 11 the reaction products are cooled.

Portions 11 and 12 are filled in general with inert material, while the catalyst is contained in the portion 4.

In the plant of Figure 3 there are an ethylene inlet 7 and and an oxygen inlet 8, both of which lead into a pipe 13 leading to the bundle of tubes in the reactor 1. The gases are heated before the reaction in heating zone 12 and cooled after the reaction in cooling zone 11 by means of a fluid which circulated in a pipe 18 between zones 11 and 12 by means of a pump 30.

The gases leaving the reactor through a pipe 14 are fed to a column 5 wherein ethylene oxide is absorbed by a liquid introduced through a pipe 15.

The gases not absorbed by the liquid leave the column 5 as overhead product and in part are discharged through a pipe 9 and in part are recycled *via* a compressor 6 and the pipe 13 to the reactor 1.

Heat developed during the reaction is removed by a fluid circulated in a pipe 16 by means of a pump 3 so producing steam in an evaporator 2. The steam is removed in a pipe 17.

The removal of the heat of reaction can be effected either by means of a circulating fluid or by an evaporating liquid other than water or by water evaporating directly in the reactor shell.

In this way it is possible to control easily the heat development and the reaction course.

In Figures 5 and 6 are shown some variants of the plant in which the process of the present invention can be carried out.

The apparatus of Figure 3 has a reactor having a shell in which are located a bundle of tubes; the tubes are connected at their ends to two plates 19 and 20 to which by flanging or welding the end caps 21 and 22 are joined. The tubes are filled with an inert solid material at their two end regions 11 and 12 and in the intermediate portion 4 they are filled with the catalyst.

The bundle of tubes is covered by a shell and the interior of the shell is divided by two baffles 23 and 24 into three distinct portions corresponding to the three portions 12, 4 and 11 of the tubes. In the tubular zone 11, the inert filling can be absent.

The apparatus also includes a pipe 18 through which a liquid circulates between the heating zone 12 and the cooling zone 11. The circulation is ensured by the pump 10.

There is also a cooling circuit 16 for the reaction zone 4 of the reactor 1; the fluid circulating in pipe 16 removes heat from the reaction zone 4 and utilizes it in the evaporator 2 for producing steam in pipe 17. The circulation in pipe 16 is ensured by the pump 3. In the pipe 16 the liquid can be an evaporating liquid, in which case both the pump 3 and the evaporator 2 can be dispensed with.

In Figure 5 there is shown a modification of the apparatus of Figure 3; in Figure 5 the heat exchanger 11 is outside the reactor 1, and may or may not contain a filling of inert material. The exchanger 11 in the apparatus of Figure 5 has the same function as the cooling zone 11 in the apparatus of Figure 3. In Figure 4 there is shown a tube of the reactor of Figure 5 having a zone 12 filled with inert materials in which the gases are heated, and a zone 4 filled with the catalyst.

In Figure 6 there is shown a further variant of the apparatus, there being present in this case more than one cooling zone and more than one heating zone. The Figure is self-explanatory and does not need therefore further clarification.

The following Example illustrates the present invention.

EXAMPLE.

To an apparatus of the type shown in Figure 3 were fed, at different times, three mixtures. The composition of the feed mixtures, the reaction conditions and the results obtained are reported in the following Table.

TABLE

Feed mixture	1st mixture	2nd mixture	3rd mixture
Ethylene	20% by volume	22% by volume	22% by volume
Oxygen	8 ,, ,,	15 ,, ,,	18 ,, ,,
Carbon dioxide	10 ,, ,,	10 ,, ,,	10 ,, ,,
Nitrogen	37 ,, ,,	32 ,, ,,	30.2 ,, ,,
Argon	25 ,, ,,	21 ,, ,,	19.8 ,, ,,
Reaction temperature (°C)	235	235	235
Temperature at the reactor inlet (°C)	180	45	45
Pressure at the reactor inlet (ata)	20	22	22
Concentration (by volume) of ethylene oxide in the reaction product at the exit of the reactor	2.8%	5.2%	6.9%

WHAT WE CLAIM IS:—

1. A process for producting an epoxide by partially oxidizing an ethylenically unsaturated compound in the vapour phase with oxygen or a gaseous mixture including oxygen, which process comprises (a) passing a mixture of (i) the ethylenically unsaturated compound and (ii) oxygen or a gaseous mixture including oxygen through a heating zone containing bodies of inert materials, so as to cause, by means of heat exchange, the temperature of the mixture of (i) and (ii) to be in the range from 100°C to 300°C; (b) passing the heated mixture through a reaction zone which contains an oxidation catalyst and in which the oxidation of the ethylenically unsaturated compound is carried out, the reaction zone being contiguous to the heating zone without any break in continuity; and (c) passing the resulting reaction products from the reaction zone through a cooling zone in which the products are cooled by means of heat exchange to a temperature lower than 150°C, the cooling zone being contiguous or not contiguous to the reaction zone and containing or not containing bodies of inert material, and the heat withdrawn in the cooling zone being utilized in the heating zone.

2. A process as claimed in Claim 1, wherein the concentration of oxygen in the mixture of (i) and (ii) is up to 20% by volume.

3. A process as claimed in Claim 1 or 2, wherein the voids between the bodies of inert material in the heating and cooling zones constitute less than 50% of the volume of the respective zone.

4. A process as claimed in Claim 1, 2 or 3, wherein the bodies of inert material are constituted by small cylinders.

5. A process as claimed in Claim 1, 2 or 3, wherein the bodies of inert material are constituted by small spheres.

6. A process as claimed in Claim 1, 2 or 3, wherein the bodies of inert material are constituted by Raschig rings.

7. A process as claimed in any preceding claim, wherein the heating zone is constituted by a bundle of tubes.

8. A process as claimed in any preceding claim, wherein the reaction zone is constituted by a bundle of tubes.

9. A process as claimed in any preceding claim, wherein the cooling zone is constituted by a bundle of tubes.

10. A process as claimed in any preceding claim, wherein the heating zone, the reaction zone and the cooling zone are constituted by portions of the same bundle of tubes.

11. A process as claimed in any one of Claims 7 to 10, wherein the ratio between the maximum dimension of one of the bodies of inert material and the internal diameter of the tubes of the bundle of tubes is not greater than 0.40:1.

12. A process as claimed in Claim 11, wherein said ratio is in the range from 0.30:1 to 0.36:1.

13. A process according to any preceding claim, wherein the process is carried out in an apparatus which comprises a reactor having a shell in which is located a bundle of tubes, divided by two or more baffles into three or more zones, the bundle of tubes having its ends terminating in plates to which the shell end caps are joined, there being a cooling circuit for an intermediate zone and one or more circuits for heating a zone at one end region of the reactor at the expense of heat withdrawn during cooling a zone at the other end region of the reactor, those regions of the tubes in the intermediate zone being filled with catalyst, those regions of the tubes in the heating zone(s) being filled with inert material and those regions of the tubes in the cooling zone(s) being filled or not filled with inert material.

14. A process according to claim 13, wherein the reactor is divided by two baffles into three zones, and wherein a circuit is provided for conveying a heat transfer fluid from the uppermost zone to the lowermost zone and back to the uppermost zone.

15. A process according to claim 13, wherein the reactor is divided by 2N baffles into 2N+1 zones, where N is an integer greater than 1, and wherein one circuit links the uppermost and lowermost zones, and another circuit links the zone adjacent the lowermost zone with the zone adjacent the uppermost zone, and, where N exceeds 2, one or more additional circuits each link corresponding heating and cooling zones.

16. A process according to any one of Claims 1 to 12, wherein the process is carried out in an apparatus which comprises a reactor having a shell in which is located a bundle of tubes, divided by a baffle into two zones, the bundle of tubes having its ends terminating in plates to which the shell end caps are joined, there being a cooling circuit for the upper zone and a circuit for heating the lower zone at the expense of heat withdrawn during cooling of reaction products at a point downstream of the reactor, those regions of the tubes in the upper zone being filled with catalyst and those regions of the tubes in the lower zone being filled with inert material.

17. A process according to any one of Claims 13 to 16, wherein the process is carried out in an apparatus which includes pumps for circulating the cooling and heating fluids.

18. A process according to any one of Claims 13 to 17, wherein said cooling circuit contains an evaporating fluid.

19. A process according to Claim 13, wherein the apparatus is substantially as hereinbefore described with reference to, and as

illustrated in Figures 2 and 3 of the accompanying drawings.

20. A process according to Claim 16, wherein the apparatus is substantially as hereinbefore described with reference to, and as illustrated in Figures 4 and 5 of the accompanying drawings.

21. A process according to Claim 15, wherein the apparatus is substantially as hereinbefore described with reference to, and as illustrated in, Figure 6 of the accompanying drawings.

22. A process according to Claim 1, substantially as described in the foregoing Example.

23. A process according to any one of Claims 1 to 21, wherein the ethylenically unsaturated compound is ethylene which is to be partially oxidized to ethylene oxide.

24. An ethylenically unsaturated compound whenever partially oxidized by a process as claimed in any preceding claim.

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1976. Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from which copies may be obtained.

1449091 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 1

FIG. 1

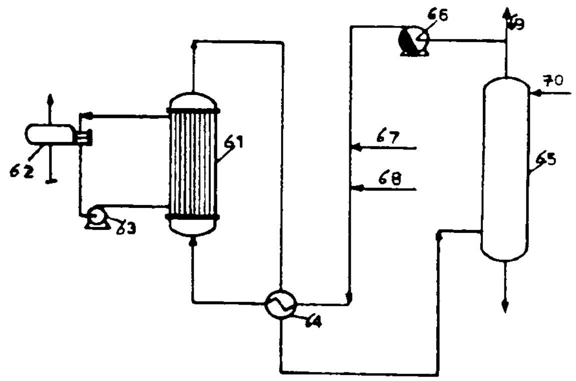

FIG. 2

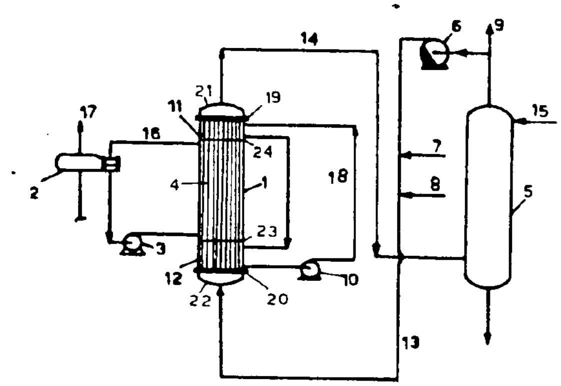

FIG. 3

1449091 COMPLETE SPECIFICATION

3 SHEETS *This drawing is a reproduction of the Original on a reduced scale*

Sheet 2

FIG. 4

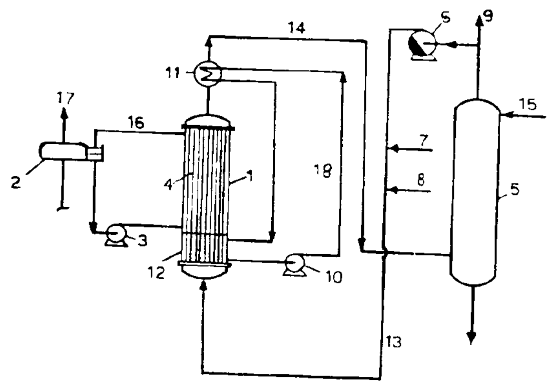

FIG. 5

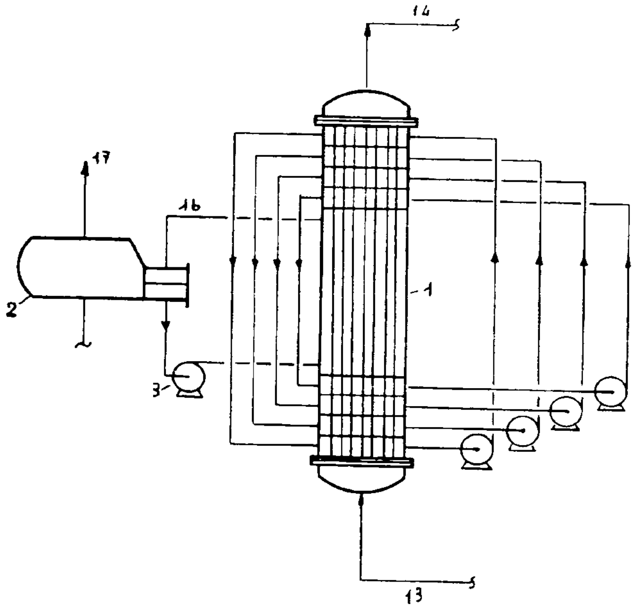

FIG.6